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明 細 書

1. 発明の名称

インクジェットプリンタ用の耐熱インク

2. 特許請求の範囲

(1) 顔料色を有するガラス系成分と溶剤とバインダと導電性付与剤とを含むインクジェットプリンタ用のインクであって、前記ガラス系成分として金属アルコキシドの加水分解固形物が配合されてなることを特徴とするインクジェットプリンタ用の耐熱インク。

(2) 金属アルコキシドの有色の加水分解固形物が、平均粒子径 $0.6\mu\text{m}$ 以下でかつ最大粒子径 $2\mu\text{m}$ 以下の微粒子であり、かつ該微粒子の融点が被印刷物の耐熱温度範囲内にあるものである特許請求の範囲第1項記載のインクジェットプリンタ用の耐熱インク。

(3) 顔料と顔料分散剤とガラス系成分と溶剤とバインダと導電性付与剤とを含むインクジェットプリンタ用のインクであって、前記ガラス系成分として金属アルコキシドの加水分解固形物が配合

されてなることを特徴とするインクジェットプリンタ用の耐熱インク。

(4) 顔料が、平均粒子径 $0.6\mu\text{m}$ 以下でかつ最大粒子径 $2\mu\text{m}$ 以下の微粒子のものである特許請求の範囲第3項記載のインクジェットプリンタ用の耐熱インク。

(5) 金属アルコキシドの加水分解固形物が、平均粒子径 $0.6\mu\text{m}$ 以下でかつ最大粒子径 $2\mu\text{m}$ 以下の微粒子であり、かつ該微粒子の融点が被印刷物の耐熱温度範囲内にあるものである特許請求の範囲第3項記載のインクジェットプリンタ用の耐熱インク。

3. 発明の詳細な説明

(産業上の利用分野)

この発明はインクジェットプリンタ用のインクに関し、詳しくは耐熱性に優れたインクジェットプリンタ用のインク組成物に係わるものである。

(従来技術)

インクジェットプリンタはノズルからインク滴を噴射して被印刷面にインクドットを形成するこ

とにより、文字や図形を記録するノンインパクト方式のプリンタである。インクジェットプリンタは小形化が可能で運転音が小さく印刷速度も早いことからOA機器用プリンタとして使用されている他、非平坦面への印刷が可能、カラー印刷が可能等の利点を有しているため、その用途が広がりつつある。

インクジェットプリンタにおけるインクの噴射は、

- (イ) インクの連続噴出流に振動を与えてインク滴を作る連続方式、
- (ロ) 圧力パルスの発生により必要時だけインク滴を作るオンデマンド方式、
- (ハ) インク滴の発射、停止を電界により行なう電界制御方式、
- (ニ) インクを霧状にし、これをイオン流で制御するインクミスト方式、

により主として行なわれる。このようなインクジェットプリンタ用のインクに要求される性質としては、正常なインク滴を形成するのに適した粘

度は又バインダの分解による着色剤の脱落が生じ、インクジェットプリンタ用の従来のインクは高温に曝される印刷物の印刷には使えない問題点があった。

そこで、この発明は前記した従来の問題点を解決せんとしたものであって、インクに配合された着色剤やバインダが変色・分解するような高温度に印刷物が曝されても、視認性及び被印刷物に対する付着力が良好であるインクジェットプリンタ用の耐熱インクを提供することを目的とする。

又、本発明の他の目的は、インクジェットプリンタのインク噴出ノズルの目詰まりがなく、かつ導電性良好なインクジェットプリンタ用の耐熱インクを提供することにある。

(問題点を解決するための手段)

この第1発明の手段は、顔料色を有するガラス系成分と溶剤とバインダと導電性付与剤とを含むインクジェットプリンタ用のインクであって、前記ガラス系成分として金属アルコキシドの加水分解固形物が配合されてなる耐熱インクとされる。

度と表面張力、インク噴出ノズルで目詰まりを起こさない着色剤の粒子径と分散安定性、さらには電場によりインクの噴出方向を制御するのに適した導電性等が挙げられ、従来のインパクト方式のプリンタ用のインクより多くの条件を満たす必要がある。

これらの条件を満たすインクジェットプリンタ用インクとしては多数提案され、幾つかは既に実用化されている。初期は水性インクが主であったが、印刷物の耐水性を良くするために、さらには紙以外の金属、ガラス、プラスチック等へ印刷するために、溶剤系インクも開発されている。

(発明が解決しようとする問題点)

しかしながら、インクジェットプリンタ用の従来のインクは何れも着色剤である染料や顔料を樹脂バインダによって被印刷面に付着させるものであり、耐熱性については全く考慮されていない。そのため、印刷物の加工工程上あるいは加工後の使用状態において、高温に曝される場合には、染料あるいは樹脂の変質によるインクの変色、或い

前記金属アルコキシドの有色の加水分解固形物は、平均粒子径 $0.6\mu\text{m}$ 以下でかつ最大粒子径 $2\mu\text{m}$ 以下の微粒子であり、かつ該微粒子の融点は被印刷物の耐熱温度範囲内にあるものとされる。

そして、この第2発明の手段は、顔料と顔料分散剤とガラス系成分と溶剤とバインダと導電性付与剤とを含むインクジェットプリンタ用のインクであって、前記ガラス系成分として金属アルコキシドの加水分解固形物が配合されてなる耐熱インクとされる。第2発明において、前記顔料は、平均粒子径 $0.6\mu\text{m}$ 以下でかつ最大粒子径 $2\mu\text{m}$ 以下の微粒子のものとされる。前記金属アルコキシドの加水分解固形物は、平均粒子径 $0.6\mu\text{m}$ 以下でかつ最大粒子径 $2\mu\text{m}$ 以下の微粒子であり、かつ該微粒子の融点は被印刷物の耐熱温度範囲内にあるものとされる。

本発明によるインク(インク組成物)は、ガラス系成分と溶剤とバインダと導電性付与剤とを基本的な主成分とし、必要に応じ界面活性剤、防錆剤等を添加することができる。本両発明は、ガラス

系成分として金属アルコキシドの加水分解による生成固形物を用いる点に特長を有する。この生成固形物は高温においてガラス状に熔融するものであり、その成分により差異はあるが、その融点は約400℃～1600℃の範囲で選択使用される。この生成固形物は、固形物自体、あるいは固形物含有調製した溶媒を含むゾルの状態でインク成分として使用される。そして、この生成固形物は金属アルコキシドの加水分解により作るので、加水分解の処理条件により粒子の調整がし易く、インクジェットプリンタのインク噴射ノズルの細孔を詰まらせない微粒子のものを確実に得ることができる。又、金属アルコキシドの加水分解固形物は、それ自体が顔料となるに十分な着色したものがあ、着色した有色の加水分解固形物を用いる場合は、特に顔料を加える必要がない。尚、この加水分解固形物が十分な着色を呈しないものは、従来と同様にインク噴射ノズル細孔を詰まらせない微粒子の顔料が配合される。本発明に用いるガラス系成分の微粒子、即ち、金属アルコ

顔料は、例えば次表に示す通常のもので微粉末の状態 で用いられる。

表

色	顔 料
白	チタン白、亜鉛華、鉛白
黒	鉄黒、黒鉛、カーボンブラック
赤	カドミウムレッド
黄	酸化鉄黄、黄鉛、チタンエロー
緑	クロムグリーン、酸化クロム
青	群青、紺青、コバルトブルー
紫	マンガンバイオレット

インクジェットプリンタは、例えば直径数十μm程度の細径ノズルからインクを噴射した記録を行なうので、ノズル目詰まりによるトラブルを防止するために、ガラス系成分あるいは顔料の粒子径は特に考慮される。

本発明に用いる溶剤として代表的なものは、ア

キシドの加水分解固形物の微粒子は、基本的には被印刷物の耐熱温度を越えない融点のものを使用することが必須である。これは被印刷物の耐熱温度範囲内において、ガラス系成分が熔融し、冷却後の被印刷物に対する付着性を持たせることができるようにするためである。ガラス系成分は室温で印刷後、ガラス系成分の熔融温度で熱処理される。

しかし、ガラス系成分の熔融温度は低すぎても良くない。何故なら、印刷物がガラス系成分の熔融温度よりも高い温度雰囲気 に曝される場合には、印字ドットが流れ、若しくは発泡して印字が不明瞭となるからである。このため、ガラス系成分の融点は、印刷物に要求される耐熱温度よりも高いか、或いは低くともおよそ50℃以内の差であることが望ましい。この様な場合には、印刷物の曝される温度雰囲気において印字ドットが部分的に熔融することはあるが、それが乱れるまでには至らず、室温において再び明瞭で強固な印刷物となる。

ルコール系溶剤，エーテル系溶剤，エステル系溶剤，ケトン系溶剤，芳香族系溶剤が挙げられるが、実際にはインクジェットプリンタ本体の仕様、被印刷物の性質に合わせて1種類あるいは2種類以上の溶剤の混合物として調製することが望ましい。

本発明に使用されるバインダは、従来のインクジェットプリンタ用インクに使用されている樹脂であれば良いが、本発明に使用する溶剤に可溶で、しかも紙以外の金属、ガラス、セラミック等に対する接着性、耐久性において優れているものが好ましい。例えばアクリル系樹脂、フェノール系樹脂、ロジン変性系樹脂等のバインダが挙げられるが、これらに限定するものではない。

インクのノズル噴射性、鋼板等への付着性、印字の融着性、及び視認性等、インクジェットプリンタ用のインクとして諸条件を満たすためのインク成分の配合範囲は、おおよそ次の如くである。即ち、

第1発明において、

ガラス系成分	(1) ~ (40)	重量部
溶剤	(40) ~ (97)	重量部
バインダ	(2) ~ (20)	重量部
導電性付与剤	(0.2) ~ (5)	重量部

第2発明において、

顔料	(5) ~ (25)	重量部
ガラス系成分	(1) ~ (35)	重量部
溶剤	(40) ~ (97)	重量部
バインダ	(2) ~ (20)	重量部
導電性付与剤	(0.2) ~ (5)	重量部

尚、バインダの含有量は、インク組成物に対して2-20重量%の範囲が好ましいが、インク噴射ノズルからの噴射安定性、最適インクドット形成性等の点から最適量が決められる。

(作用)

第1発明において、金属アルコキシドの加水分解固形物は有色のガラス系成分であり、顔料とインク融着の両作用をなす。

第2発明において、金属アルコキシドの加水分解固形物は主としてインク融着の作用をなす。

溶液を加え、室温に冷却し、1時間攪拌を続けて白色の固形物が分散したゾル(固形分濃度10%、平均粒子径0.1、最大粒子径0.5 μ m)を得た。

次いで、メタクリル酸メチル100重量部とアゾビスイソブチルニトリル12重量部をエチルアルコール200重量部中に混合し重合を行ない、平均分子量45000のアクリル樹脂ワニスを得る。このワニス(アクリル系バインダ樹脂)2重量部及び前述の工程より得たゾル80重量部及び導電性付与剤として硝酸リチウム0.4重量部を順次配合し混合して粘度5.2cp、表面張力25dyn/cm、比抵抗880 Ω cm(何れも20 $^{\circ}$ Cの値)のインクを得た。

このインクを用い荷電制御方式のインクジェットプリンタにより、鋼板上に印字テストを行なったところ、噴射特性は良好で鋼板への付着性も良好であり、かつ鋼板上の印字は明瞭であった。次にこの印刷物を空気中で800 $^{\circ}$ C、30分間加熱した後、室温まで冷却したところ印字ドットは鋼

両発明における加水分解固形物は耐熱温度が充分高く、かつインク噴射ノズルに適した微粒子のものである。

(実施例)

次に、本発明の実施例を示す。尚、本発明は以下の実施例に限定されるものではない。

実施例1

先ず、ガラス系成分のゾルが用意される。本例1のゾルは固形物として白色の10Na₂O-20B₂O₃-10TiO₂-60SiO₂を含むものであり、以下の工程にて作られる。

エタノールに溶かしたオルトケイ酸エチルとエタノールに溶かしたアンモニア水(アンモニアはSiと当モル)を、還流冷却器を備えた所定容器内にて5時間加熱して還流させる。次いで、容器内にはナトリウムメチラート、トリエチルボレート、チタンテトライソプロポキシドの各金属アルコキシドを各所定量エタノールの所定量とともに添加し、2時間還流を続ける。しかる後、水(上記アルコキシドの3倍モル)とエタノールの混合

板上に完全に融着しており、視認性も良好であった。又、この印刷物を再び600 $^{\circ}$ Cに加熱しても印字の乱れは無かった。

実施例2

先ず、ガラス系成分のゾルが用意される。本例2のゾルは固形物として白色の35PbO-10Na₂O-15B₂O₃-10TiO₂-30SiO₂系の組成物を含むものであり、以下の工程にて作られる。

エタノールに溶かしたオルトケイ酸エチルとエタノールに溶かしたアンモニア水(アンモニアはSiと当モル)を、還流用の所定容器内にて5時間加熱して還流させる。

次いで、酢酸鉛、イソプロピルアルコール、キシレン(溶媒)、及び金属ナトリウムを4時間加熱して還流し、分液した鉛イソプロポキシドを用意し、容器内に該鉛イソプロポキシド、ナトリウムメチラート、トリエチルボレート、チタンテトラエトキシドの各金属アルコキシドを各所定量エタノールの所定量とともに添加し、2時間還流を続ける。しかる後、水(上記アルコキシドの3倍

モル)とエタノールの混合溶液を加え、室温に冷却し、1時間攪拌を続けて白色の固形物が分散したゾル(固形分濃度10%,平均粒子径0.1,最大粒子径0.5 μ m)を得た。

次いで、実施例1と同様に、バインダ(ワニス)2重量部、実施例2の前述の工程より得たゾル80重量部、硝酸リチウム0.4重量部を順次配合し混合して粘度3.9cp、表面張力26 dyne/cm、比抵抗780 Ω cm(何れも20°Cの値)のインクを得た。

このインクを用いて鋼板上に印字テストをしたところ、実施例1と同様に良好であり、鋼板上の印字は明瞭であった。又、印刷物を空気中で600°C、30分間加熱した後、室温まで冷却したところ、実施例1と同様に完全に融着し、視認性は良好であった。さらに印刷物を再び400°Cに加熱したが印字の乱れは無かった。

実施例3

先ず、ガラス系成分のゾルが用意される。本例3のゾルは固形物として無色の20Na₂O-20B₂O₃-60

順次配合し混合して粘度5.6cp、表面張力22 dyne/cm、比抵抗720 Ω cm(何れも20°Cの値)の白色のインクを得た。

このインクを用いて鋼板上に印字テストをしたところ、実施例1と同様に良好な結果が得られた。又、印刷物を空気中で800°C、30分間加熱した後、室温まで冷却したところ、実施例1と同様に鋼板に完全に付着し、視認性は良好であった。又、印刷物を再び650°Cに加熱しても印字の乱れは無かった。

実施例4

先ず、ガラス系成分のゾルが用意される。本例4のゾルは固形物として無色の35PbO-10Na₂O-15B₂O₃-40SiO₂系組成物を含むものであり、以下の工程にて作られる。

エタノールに溶かしたオルトケイ酸エチルとエタノールに溶かしたアンモニア水(アンモニアはSiと当モル)を、還流用の所定容器内にて5時間加熱し還流させる。

一方、酢酸鉛、イソプロピルアルコール、キシ

SiO₂系組成物を含むものであり、以下の工程にて作られる。

エタノールに溶かしたオルトケイ酸エチルとエタノールに溶かしたアンモニア水(アンモニアはSiと当モル)を、還流用の所定容器内にて5時間加熱して還流させる。次いで、容器内にはナトリウムメチラート、トリエチルボレーートの各金属アルコキシドを各所定量エタノールの所定量とともに添加し、2時間還流を続ける。しかる後、水(上記アルコキシドの3倍モル)とエタノールの混合溶液を加え、室温に冷却し、1時間攪拌を続けて固形物が分散したゾル(固形分濃度10%,平均粒子径0.1,最大粒子径0.5 μ m)を得た。

次いで、白色顔料粉末(帝国加工KK製造、微粒子酸化チタンMT-500B(平均粒子径約35m μ))20重量部、顔料分散剤(日本油脂KK製造、ポリスターA-1060、陰イオン系界面活性剤)0.1重量部、本例3の前記工程により得たゾル40重量部、硝酸リチウム0.8重量部、実施例1と同様なバインダ(ワニス)15重量部を

レン(溶媒)、及び金属ナトリウムを4時間加熱して還流し、分液した鉛イソプロボキシドを用意する。次いで、容器内には鉛イソプロボキシド、ナトリウムメチラート、トリエチルボレーートの各金属アルコキシドを各所定量エタノールの所定量とともに添加し、2時間還流を続ける。しかる後、水(上記アルコキシドの3倍モル)とエタノールの混合溶液を加え、室温に冷却し、1時間攪拌を続けて固形物の分散したゾル(固形分濃度10%,平均粒子径0.1,最大粒子径0.5 μ m)を得た。

次いで、実施例3と同様に、白色顔料粉末(帝国加工KK製造、微粒子酸化チタンMT-500B(平均粒子径約35m μ))20重量部、顔料分散剤(ポリスターA-1060)0.1重量部、本例4の前記工程により得たゾル40重量部、硝酸リチウム0.8重量部、及び実施例1と同様なバインダ(ワニス)15重量部を順次混合して粘度4.3cp、表面張力23 dyne/cm、比抵抗830 Ω cm(何れも20°Cの値)の白色のインクを得た。

このインクを用いてアルミ板上に印字テストをしたところ、実施例1と同様に良好な結果が得られた。又、印刷物を空気中で500℃、1時間焼成後も、印字ドットはアルミ板面に完全に融着し視認性は良好であった。又、印刷物を再び400℃に加熱しても印字の乱れはなかった。

比較例1

メタクリル酸メチル100重量部とアゾビスイソブチルニトリル12重量部をエチルアルコール200重量部中に混合し重合を行ない、平均分子量45000のアクリル樹脂ワニスを得る。このワニス30重量部と、黄色染料(BASF社のネオザボンイエローGG)6重量部、さらに硝酸リチウム1.5重量部、シリコンオイル(信越化学KK製造、KF-56)2重量部を添加して、粘度2.1cp、表面張力20dyne/cm、比抵抗750Ωcm(何れも20℃の値)のインクを調製した。

このインクを用いて鋼板上への印字テストをしたところ、実施例1と同様に良好な結果が得られた。ところが、この印刷物を250℃に加熱する

と、印字ドットが変色して視認性が非常に悪くなると同時に、指で擦ると印字が簡単に消えた。

比較例2

酸化チタン5重量部をエタノールを溶媒にして混合し、ポットミルで48時間混合・粉碎した。その後、粒子径2μm以上のものをフィルターで除去し、溶剤量を調製して固形分濃度20%の着色剤分散液とした。上記着色分散液100重量部に対し、実施例1におけるアクリル樹脂ワニス13重量部を添加し、さらに硝酸ニチウム1.5重量部、界面活性剤(住友3MKK製造、フッ素系界面活性剤FC-430)0.7重量部を添加して、粘度3.2cp、表面張力28dyne/cm、比抵抗930Ωcm(何れも20℃の値)のインクを得た。

このインクを用いて鋼板上への印字テストをしたところ、実施例1と同様に良好な結果が得られた。ところが、印刷物を250℃、30分間加熱すると、バインダの分解のために印字ドットの付着力が著しく低下し、簡単に脱落した。

(発明の効果)

本第1発明は、ガラス系成分として金属アルコキシドの有色の加水分解固形物が配合されていることより、該加水分解固形物自体が顔料の機能を有する。

本第2発明は、ガラス系成分として金属アルコキシドの加水分解固形物と顔料とが配合されていることより、所定の色のインクとされる。第1、第2の両発明において配合される加水分解固形物は、金属アルコキシドの加水分解の処理により生成されるので、処理条件の調製によりその固形物粒子は平均粒子径が0.6μm以下で、かつ最大粒子径2μm以下のものとなすことができ、インクジェットプリンタのインク噴射ノズルの目詰まりを生じさせない。

又、第1、第2の両発明において、被印刷物に印刷されるインクはバインダにより付着し、付着したインクは熱処理によりガラス系成分が被印刷物に融着する。ガラス系成分は耐熱性であり、ガラス系成分の融点以下の温度の加熱では印字ドッ

トの視認性の低下及び剥がれを生じない。即ち、本両発明のインクはインクジェットプリンタのインク噴出ノズルの目詰まりがなく、かつ導電付与剤が配合されているので導電性の条件を満たし、印字の形成が良好であり、又、ガラス系成分が配合されていることより、着色剤やバインダが変色、分解する高温において印字の視認性及び付着力を良好にすることができる。

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1. Title of the Invention

Heat-resistant Ink for Ink Jet Printers

2. What is claimed is:

(1) A heat-resistant ink for ink jet printers, comprising: a glass component containing a pigment color, a solvent, a binder and an electro-conductive additive, characterized in that a solid matter obtained by hydrolysis of a metal alkoxide is blended as the glass component.

(2) The heat-resistant ink for ink jet printers according to claim 1, characterized in that the colored solid matter obtained by hydrolysis of the metal alkoxide is in the form of fine particles having an average particle diameter of 0.6 μm or less, with a maximum particle diameter of 2 μm or less, and the melting point of the fine particles falls within a heat-resistant temperature range of a material to be printed.

(3) A heat-resistant ink for ink jet printers, comprising: a pigment, a pigment dispersant, a glass component, a solvent, a binder and an electro-conductive additive, characterized in that a solid matter obtained by hydrolysis of a metal alkoxide is blended as the glass component.

(4) The heat-resistant ink for ink jet printers, according to claim 3, characterized in that the pigment is in the form of fine particles having an average particle diameter of 0.6 μm or less, with a maximum particle diameter of 2 μm or less.

(5) The heat-resistant ink for ink jet printers, according to claim 3,

characterized in that the matter obtained by hydrolysis of the metal alkoxide is in the form of fine particles having an average particle diameter of 0.6 μ m or less, with a maximum particle diameter of 2 μ m or less, and the melting point of the fine particles falls within a heat-resistant temperature range of a material to be printed.

3. Detailed Description of the Invention

(Field of the Industrial Use)

The present invention relates to an ink for ink jet printers, and more specifically to an ink composition for ink jet printers, which has an excellent heat resisting property.

(Prior Art)

Ink jet printers are printers of a non-impact type in which characters and figures are printed by jetting ink drops from the nozzle to form ink dots on a surface of a sheet to be printed. Ink jet printers can be made small in size, generate small driving noise and have a high printing speed. Due to such advantages, they are presently used as printers for OA equipments. Further, these printers have such advantages that it is possible to print on non-flat surfaces and to print in colors, etc., and therefore their usage is expanding.

In the ink jet printers, the jetting of ink is performed mainly in the following systems:

(a) the continuous system in which ink drops are created by vibrating the continuous jet flow of ink;

(b) the on-demand system in which ink drops are created only when necessary by generating the pressure pulse;

(c) the electrical field control system in which the jetting of ink drops and stopping thereof are performed by means of the electrical field; and

(d) the ink mist system in which ink is atomized and ink mist is controlled by ion flow. The properties required for ink for such ink jet printers are appropriate viscosity and surface tension for forming normal ink drops, such particle diameter and dispersion stability of the coloring agent that do not cause clogging in the ink jet nozzle, appropriate electro-conductivity for controlling the

ink jetting direction by the electrical field, etc. Thus, as compared to the ink for the conventional impact-type printers, it is necessary to satisfy more conditions.

There have been proposed a great number of types of inks for ink jet printers that satisfy these conditions, and some of them have been already developed for actual use. In the beginning, the water-based ink was mainly used, but now the solvent-based ink is being developed in order to improve the water-resistant property of the printed material, or to be able to print on a material other than paper, such as metal, glass or plastic.

(Problem to be Solved by the Invention)

However, all of the conventional inks for ink jet printers are of such type that dyes or pigments, which serve as coloring agents, are attached to a surface of a material to be printed, and here, the heat resistance is not considered at all. Therefore, when the printed material is exposed to a high temperature while the material is being processed or used for its purpose after being processed, the deterioration of the dyes or resin occurs to cause fading, or the decomposition of the binder occurs to cause dropping-off of the coloring agent. Under these circumstances, the conventional inks for ink jet printers entail such drawback that they cannot be used for the printing of materials which are to be exposed to high temperatures.

The present invention has been proposed as a solution to the above-described drawbacks of the prior art techniques, and an object thereof is to provide a heat-resistant ink for ink jet printers, which has an excellent recognizability and an excellent attachment to the to-be-printed material even if the printed material is exposed to such a high temperature that the coloring agents and binder blended to the ink are faded or decomposed.

Another object of the present invention is to provide a heat-resistant ink for ink jet printers, which does not cause clogging in the ink jet nozzle of the ink jet printer and has an excellent electro-conductivity.

(Means for Solving the Problem)

The means of the first invention is an ink for ink jet printers, comprising: a glass component having a pigment color, a solvent, a binder and an electro-conductive additive, and a solid matter obtained by hydrolysis of a metal

alkoxide is blended as the glass component to make a heat-resistant ink.

The colored solid matter obtained by hydrolysis of the metal alkoxide is in the form of fine particles having an average particle diameter of 0.6 μ m or less, with a maximum particle diameter of 2 μ m or less, and the melting point of the fine particles falls within a heat-resistant temperature range of a material to be printed.

The means of the second invention is an ink for ink jet printers, comprising: a pigment, a pigment dispersant, a glass component, a solvent, a binder and an electro-conductive additive, and a solid matter obtained by hydrolysis of a metal alkoxide is blended as the glass component to make a heat-resistant ink. In the second invention, the pigment is in the form of fine particles having an average particle diameter of 0.6 μ m or less, with a maximum particle diameter of 2 μ m or less. Further, the solid matter obtained by hydrolysis of the metal alkoxide is in the form of fine particles having an average particle diameter of 0.6 μ m or less, with a maximum particle diameter of 2 μ m or less, and the melting point of the fine particles falls within a heat-resistant temperature range of a material to be printed.

The ink (ink composition) of the present invention contains, as its basic main ingredients, a glass component, a solvent, a binder and an electro-conductive additive, and in accordance with necessity, a surfactant, a rust inhibitor, etc. may be added thereto. Both of the present inventions are characterized in the aspect that a solid matter produced by hydrolysis of a metal alkoxide is employed as the glass component. The produced solid matter is of such a type that is fused in a glass-like manner at a high temperature. The melting point of the solid matter, though it varies depending on its components, is selected to fall within a range of about 400°C to 1600°C when used. The solid matter is used as an ink component as the matter itself or in the form of sol including a solvent prepared to contain the solid matter. Since the solid matter is formed by hydrolysis of a metal alkoxide, it is easy to adjust the form of

particles by varying the processing conditions for the hydrolysis. Therefore, such fine particles that do not block minute pores of the ink jet nozzle of an ink jet printer can be obtained reliably. Further, some of the solid matters are sufficiently colored to serve as pigments by themselves, and when such a colored solid matter is employed, it is not particularly necessary to add a pigment. On the other hand, in the case where the solid matter employed is of such a type that does not exhibit a color in a sufficient strength, a pigment of such fine particles that do not block minute pores of an ink jet nozzle is blended as in the conventional technique. Here, it is essential to use fine particles of the glass component, that is, fine particles of the solid matter obtained by hydrolysis of the metal alkoxide base, of basically such a type having a melting point that does not exceeds the heat-resistant temperature of the material to be printed. This is because the glass component is fused within the heat-resistant temperature range of the material to be printed and thus after cooled down, an adhesion to the material to be printed can be imparted. The glass component is heat-processed at the melting point of the glass component after printing at room temperature.

However, the melting point of the glass component should not be excessively low for the following reason. In the case where the printed material is exposed to such an atmosphere of a temperature higher than the melting point of the glass component, print dots fuse off or foam to make the printing unclear. In order to avoid this, the melting point of the glass component should preferably be higher than the heat-resistant temperature required for the printed material, or within a difference of 50°C at the lowest. In such case, print dots may partially fuse in the atmosphere of the temperature to which the printed material is exposed; however they will not reach the point where the print is visually disturbed. At room temperature, it restores a clear and solid printed material.

Examples of the pigment are ordinary types such as listed in Table below, and as mentioned above, the pigment is used in the form of fine particles.

TABLE

Color	pigment
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White	titanium white, zinc white, white lead
black	iron black, graphite, carbon black
red	cadmium red
yellow	iron oxide yellow, chrome yellow, titanellow
green	chrome green, chromium oxide
blue	ultramarine blue, Prussian blue, cobalt blue
purple	manganese violet

Since ink jet printers carry out printing by jetting the ink from a nozzle with micro-pores having a diameter of, for example, about several tens of micrometers, the diameter of the particles of the glass component or pigment is particularly considered in order to prevent troubles caused by blocking of the nozzle pores.

Typical examples of the solvent used for the present invention are alcohol-based solvents, ether-based solvents, ester-based solvents, ketone-based solvents and aromatic-based solvents. In practice, one type or a mixture of two or more types of solvents should be prepared in accordance with the specification of the ink jet printer used, and the properties of the material to be printed.

The binder used for the present invention may be any arbitrary type of resin that is used in the conventional inks for ink jet printers. However, it is preferable that such a type that is soluble to the solvent used in the present invention and at the same time, excellent in adhesion with respect to materials other than paper, such as metals, glass and ceramics, and in durability should be used. Example of such a binder are acryl-based resins, phenol-based resin and rosin denatured resins, but the invention is not limited to these.

The range of blending the ink component to satisfy various conditions as an ink for ink jet printer, that is, namely, the nozzle jetting property of the ink, adhesion of the ink to a steel plate or the like, the fusion bond of printed matter and the recognizability of printed material are approximately as follow.

That is:

In the first invention,

Glass component	(1) to (40) parts by weight
Solvent	(40) to (97) parts by weight
Binder	(2) to (20) parts by weight
Electro-conductive additive	(0.2) to (5) parts by weight

In the second invention,

Pigment	(5) to (25) parts by weight
Glass component	(1) to (35) parts by weight
Solvent	(40) to (97) parts by weight
Binder	(2) to (20) parts by weight
Electro-conductive additive	(0.2) to (5) parts by weight

It should be noted that the preferable content of the binder is in a range of 2 to 20% by weight with respect to the amount of the ink composition, and the optimal amount thereof is decided in the light of the jet stability of the ink jet nozzle, the optimal ink dot formability and the like.

(Operation)

In the first aspect of the invention, the solid matter obtained by hydrolyzed of the metal alkoxide is a colored glass component, and it functions as both of a pigment and a fusion bond of ink.

In the second aspect of the invention, the hydrolyzed solid matter obtained by hydrolyzed of the metal alkoxide functions mainly as a fusion bond of ink.

In both aspects of the invention, the hydrolyzed solid matter is in the form of fine particles having a sufficiently high heat-resistant temperature and suitable for the ink jet nozzle.

(Examples)

Examples of the present invention will now be described. It should be noted here that the present invention is not limited to the following examples.

Example 1

First, a sol of the glass component was prepared. The sol of Example 1 contained a white solid matter of $10\text{Na}_2\text{O}-20\text{B}_2\text{O}_3-10\text{TiO}_2-60\text{SiO}_2$, which was formed in the following steps.

That is, ethyl orthosilicate dissolved into ethanol and ammonium water dissolved into ethanol (ammonium being equimolar to Si) were heated within a predetermined container equipped with a circulating current cooler for 5 hours and circulate the current. Then, a predetermined amount of each of metal alkoxides of sodium methylate, triethyl borate and titanium tetraisopropoxide was added with a respective predetermined amount of ethanol into the container and the circulation of current was continued for 2 hours. After a while, a mixture solution of water (in amount of molar 3 times as much as that of the alkoxide) and ethanol was added thereto and the resultant was cooled down. Then, the solution was stirred for 1 hour, and thus a sol in which the white solid matter was dispersed (the concentration of the solid matter: 10%, the average particle diameter $0.1\mu\text{m}$, and the maximum particle diameter $0.5\mu\text{m}$) was obtained.

Subsequently, 100 parts by weight of methyl methacrylate and 12 parts by weight of azobisisobutyronitrile were mixed into 200 parts by weight of ethyl alcohol for polymerization, and thus an acryl resin varnish having an average molecular weight of 45000 was obtained. 2 parts by weight of thus obtained varnish (acryl-based binder resin), 80 parts by weight of the sol obtained by the above-described step and 0.4 parts by weight of lithium nitrate, which would serve as the electro-conductive additive, were mixed one after another and thus an ink having a viscosity of 5.2cp, a surface tension of 25 dyne/cm and specific resistance of $880\Omega\text{cm}$ (all values measured at a temperature of 20°C) was obtained.

The thus obtained ink was subjected to printing test on a steel plate using an ink jet printer of an electrical charge control mode. The results indicated that the jetting property and the adhesion to the steel plate were both good, and the printing on the steel plate was clear. After that, the printed material was heated in the air at 800°C for 30 minutes and cooled down to room temperature, but the print dots were completely fusion-bonded onto the steel plate and the recognizability was also good. Further, the printed material was once again heated to 600°C , but the printing was not disturbed.

Example 2

First, a sol of the glass component was prepared. The sol of Example 2 contained a white solid matter of $35\text{PbO}-10\text{Na}_2\text{O}-15\text{B}_2\text{O}_3-10\text{TiO}_2-30\text{SiO}_2$, which was formed in the following steps.

That is, ethyl orthosilicate dissolved into ethanol and ammonium water dissolved into ethanol (ammonium being equimolar to Si) were heated within a predetermined container equipped with a circulating current cooler for 5 hours and circulate the current.

Next, lead citrate, isopropylalcohol, xylene (sovent) and sodium metal were heated for 4 hours to circulate the current. Then, a portion of the thus obtained lead isopropoxide was separated. After that, the portion of lead isopropoxide, and a predetermined amount of each of metal alkoxides of sodium methylate, triethyl borate and titanium tetraisopropoxide was added with a respective predetermined amount of ethanol into the container and the circulation of current was continued for 2 hours. After a while, a mixture solution of water (in amount of molar 3 times as much as that of the alkoxide) and ethanol was added thereto and the resultant was cooled down. Then, the solution was stirred for 1 hour, and thus a sol in which the white solid matter was dispersed (the concentration of the solid matter: 10%, the average particle diameter $0.1\mu\text{m}$, and the maximum particle diameter $0.5\mu\text{m}$) was obtained.

Subsequently, as in the case of Example 1, 2 parts by weight of the binder (vanish), 80 parts by weight of the sol obtained by the above-described step of Example 2 and 0.4 parts by weight of lithium nitrate, were mixed one after another and thus an ink having a viscosity of 3.9cp, a surface tension of 26 dyne/cm and specific resistance of $780\Omega\text{cm}$ (all values measured at a temperature of 20°C) was obtained.

The thus obtained ink was subjected to printing test on a steel plate, and the results were as excellent as those of Example 1, and the printing on the steel plate was clear. After that, the printed material was heated in the air at 600°C

for 30 minutes and cooled down to room temperature, but the print dots were completely fusion-bonded onto the steel plate as in the case of Example 1 and the recognizability was also good. Further, the printed material was once again heated to 400°C, but the printing was not disturbed.

Example 3

First, a sol of the glass component was prepared. The sol of Example 3 contains a non-colored solid matter of $20\text{Na}_2\text{O}-20\text{B}_2\text{O}_3-60\text{SiO}_2$, which was formed in the following steps.

That is, ethyl orthosilicate dissolved into ethanol and ammonium water dissolved into ethanol (ammonium being equimolar to Si) were heated within a predetermined container equipped with a circulating current cooler for 5 hours and circulate the current. Then, a predetermined amount of each of metal alkoxides of sodium methylate and triethyl borate was added with a respective predetermined amount of ethanol into the container and the circulation of current was continued for 2 hours. After a while, a mixture solution of water (in amount of molar 3 times as much as that of the alkoxide) and ethanol was added thereto and the resultant was cooled down. Then, the solution was stirred for 1 hour, and thus a sol in which the white solid matter was dispersed (the concentration of the solid matter: 10%, the average particle diameter 0.1 μm , and the maximum particle diameter 0.5 μm) was obtained.

Subsequently, 20 parts by weight of white pigment powder (micro-particle titanium oxide MT-500B (having an average particle diameter of about 35 μm), manufactured by Teikoku Kakou KK), 0.1 part by weight of pigment dispersant (Polyster - A - 1060, negative ion-based surfactant manufactured by NOF corporation), 40 parts by weight of the sol obtained by the above-described step of Example 3, 0.8 parts by weight of lithium nitrate and 15 parts by weight of binder (vanish) similar to that used in Example 1, were mixed one after another and thus a white ink having a viscosity of 5.6cp, a surface tension of 22 dyne/cm and specific resistance of 720 Ωcm (all values measured at a temperature of

20°C) was obtained.

The thus obtained ink was subjected to printing test on a steel plate, and the results were as excellent as those of Example 1. After that, the printed material was heated in the air at 800°C for 30 minutes and cooled down to room temperature, but the print dots were completely fusion-bonded onto the steel plate as in the case of Example 1 and the recognizability was also good. Further, the printed material was once again heated to 650°C, but the printing was not disturbed.

Example 4

First, a sol of the glass component was prepared. The sol of Example 3 contains a non-colored solid matter of $35\text{PbO}-10\text{Na}_2\text{O}-15\text{B}_2\text{O}_3-40\text{SiO}_2$, which was formed in the following steps.

That is, ethyl orthosilicate dissolved into ethanol and ammonium water dissolved into ethanol (ammonium being equimolar to Si) were heated within a predetermined container equipped with a circulating current cooler for 5 hours and circulate the current.

Meanwhile, lead citrate, isopropylalcohol, xylene (solvent) and sodium metal were heated for 4 hours to circulate the current. Then, a portion of the thus obtained lead isopropoxide was separated. After that, a predetermined amount of each of metal alkoxides of lead isopropoxide, sodium methylate and triethyl borate was added with a respective predetermined amount of ethanol into the container and the circulation of current was continued for 2 hours. After a while, a mixture solution of water (in amount of molar 3 times as much as that of the alkoxide) and ethanol was added thereto and the resultant was cooled down. Then, the solution was stirred for 1 hour, and thus a sol in which the white solid matter was dispersed (the concentration of the solid matter: 10%, the average particle diameter $0.1\mu\text{m}$, and the maximum particle diameter $0.5\mu\text{m}$) was obtained.

Subsequently, as in Example 3, 20 parts by weight of white pigment

powder (micro-particle titanium oxide MT-500B (having an average particle diameter of about 35 μ m), manufactured by Teikoku Kakou KK), 0.1 part by weight of pigment dispersant (Polyster - A - 1060, negative ion-based surfactant manufactured by NOF corporation), 40 parts by weight of the sol obtained by the above-described step of Example 4, 0.8 parts by weight of lithium nitrate and 15 parts by weight of binder (vanish) similar to that used in Example 1, were mixed one after another and thus a white ink having a viscosity of 4.3cp, a surface tension of 23 dyne/cm and specific resistance of 830 Ω cm (all values measured at a temperature of 20°C) was obtained.

The thus obtained ink was subjected to printing test on an aluminum plate, and the results were as excellent as those of Example 1. After that, the printed material was backed in the air at 500°C for 1 hour, the print dots were completely fusion-bonded onto the aluminum plate and the recognizability was also good. Further, the printed material was once again heated to 400°C, but the printing was not disturbed.

Comparative Example 1

100 parts by weight of methyl methacrylate and 12 parts by weight of azobisisobutylnitril were mixed into 200 parts by weight of ethyl alcohol to cause polymerization, and thus an acryl resin vanish having an average molecular weight of 45000 was obtained. Then, 30 parts by weight of this vanish, 6 parts by weight of yellow dye (Neo-zamboa yellow GG manufactured by BASF), 1.5 parts by weight of lithium nitrate and 2 parts by weight of silicon oil (KF-56 manufactured by Shin Etsu Chemical Co. Ltd.) were added and thus an ink having a viscosity of 2.1cp, a surface tension of 20 dyne/cm and specific resistance of 750 Ω cm (all values measured at a temperature of 20°C) was obtained.

The thus obtained ink was subjected to printing test on a steel plate, and the results were as excellent as those of Example 1. However, if the printed

material was heated to 250°C, the print dots were faded and the recognizability was very much degraded. At the same time, when the print dots were scrubbed with a finger, they were easily erased.

Comparative Example 2

5 parts by weight of titanium oxide was mixed using ethanol as a solvent, and the resultant was mixed and ground in a pot mill for 48 hours. After that, particles of a diameter of 2 μ m were removed with a filter, and the amount of solvent was adjusted. Thus, a coloring dispersant solution having a concentration of solid matter of 20% was prepared. To 100 parts by weight of the coloring dispersant solution, 13 parts by weight of the acryl resin vanish used in Example 1, 1.5 parts by weight of lithium nitrate and 0.7 parts by weight of surfactant (fluorine-based surfactant FC-430 manufactured by Sumitomo 3M Limited) were added and thus an ink having a viscosity of 3.2cp, a surface tension of 28 dyne/cm and specific resistance of 930 Ω cm (all values measured at a temperature of 20°C) was obtained.

The thus obtained ink was subjected to printing test on a steel plate, and the results were as excellent as those of Example 1. However, if the printed material was heated at 250°C for 30 minutes, the decomposition of the binder occurred, and the attachment strength of the print dots were significantly lowered. Therefore, the dots drop off easily.

(Advantages of the Invention)

According to the first aspect of the present invention, a colored solid matter obtained by hydrolysis of a metal alkoxide is blended as the glass component, and the solid matter obtained by the hydrolysis itself has a function of a pigment.

According to the second aspect of the present invention, a solid matter obtained by hydrolysis of a metal alkoxide as the glass component and a pigment are blended together, to prepare an ink of a predetermined color. The hydrolysis solid matter blended in each of the first and second aspects of the

present invention is formed by hydrolysis of a respective metal alkoxide. Therefore, by adjusting the processing conditions, the solid matter can be prepared in the form of fine particles having an average particle diameter of 0.6 μ m or less, with a maximum particle diameter of 2 μ m or less. In this manner, it is possible to prevent the clogging in the ink jet nozzle of the ink jet printer.

Further, in both of the first and second aspects of the invention, the ink to be printed on a print material is attached thereto by means of the binder, and the ink is attached to the print material as the glass component thereof is fusion-bonded thereby by heat treatment. The glass-based component is heat-resisting and therefore at a temperature no higher than the melting point of the glass component, the recognizability of the print dots does not deteriorates, or the dropping off of the print dots does not occur. That is, the ink of each of the aspects of the invention does not have a problem of clogging in the ink jet nozzle of the ink jet printer. At the same time, the ink satisfies the condition of electro-conductivity since an electro-conductive additive is blended thereto. Thus, the forming of print characters is excellent. Further, the glass-based component is added to the ink, and therefore the recognizability of the print and the attachment thereof can be maintained excellent even at such a high temperature that conventional coloring agents and binders fade and decompose.

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